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NEW LOW TEMPERATURE PROCESSING FOR BORON

CARBIDE/ALUMINUM BASED COMPOSITE ARMOR

FINAL REPORT

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The developed B_4C/Al based materials are a promising alternative for the use in lightweight armor application. The advantage of B_4C/Al composite over the traditional metal armor is its ballistic limit of 80 to 90% of that for hot pressed B_4C, thus similar to ceramics such as AlN or SiC. The advantage of B_4C/Al over monolithic ceramic armor is its higher toughness. The ballistic efficiency of B_4C/Al materials, relative to hot-pressed boron carbide, was found to be directly related to the initial boron carbide content, the B-C-Al phases formed in situ, and their continuity. The highest improvement of ballistic efficiency was associated with increasing contents of B_4C and AlB_2 in the system.

The Rapid Omnidirectional Compaction process is a suitable technique to produce nearly dense B_4C/Al cermet at the low temperature. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like structure through heat-treatment. Mechanical properties of B_4C/Al cermets depend mostly on the concentration and continuity of the boron carbide phase. Colloidal processing and post densification heat-treatment can be used to

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19. further modify properties for the application at hand.

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INTRODUCTION

Boron carbide/aluminum composites combine a ceramic's hardness, stiffness, and low density with a metal's ability to dissipate tensile stress. One of the limitations of any B_4C/Al cermet fabrication process is that the starting composition must always have an excess of metal. In order to produce armor materials, this metal must be depleted by formation of various binary and ternary phases. Depending on the extent of heat-treatment. 20 to 40 % of the material will consist of these new phases. It is not surprising therefore, that these phases play a critical role in the mechanical behavior of the composite, and one would expect that the ballistic performance of these multi-phase composites would vary greatly, depending on material chemistry.

The objective of this work was to develop the ability, starting with a given powder composition, to vary the fabrication conditions in such a manner that a series of B_4C/Al materials with controlled chemistry could be produced. The tests conducted on these materials resulted in determination of the ballistic limits for B_4C/Al materials as well as in the optimization of the material chemistry with respect to ballistic behavior.

With the Rapid Omnidirectional Compaction process, employed in this work, densification of boron carbide and aluminum is done near the melting point of aluminum, suppressing the formation of a low temperature phases and eliminating formation of high temperature phases. Thus, one can fabricate the cermet by ROC with minimal formation of B-C-Al phases, and then post-heat treat to form multi-phase ceramic-like structures with variety of designed compositions.

In the ROC fabrication technique two basic types of B_4C/Al materials can be made. The first with isolated B_4C grains in the multi-phase ceramic-metal matrix and the second with continuous phases of ceramic and metal. Both processes, described in detail in Appendix A, have similar basic processing stages. The "preforms" are densified into parts by heating them to a temperature near the melting point of aluminum in a composite fluid die material, and then by applying pressure to them for less than one minute. The "fluid" glass die exhibits plastic flow at the temperature and pressure of densification. The die walls function as incompressible fluid elements, which transmit an isostatic pressure of up to 120 ksi to the part.

Obtaining dense B_4C/Al materials requires development of processing procedures, including mixing of ceramic and metal powders, formation of greenware, sample encapsulation and degassing, and densification under rapidly applied high pressure. Therefore, the research concentrated on the following areas:

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1.0. Preparation and Properties of ROCed Cermets
2.0. Post heat-treatment.
3.0. Ballistic evaluation.
4.0 Gradient structures.

1.0. PREPARATION AND PROPERTIES OF ROCED CERMETS

The objectives of this portion of the project were (i) development of dry and wet powder processing methods for mixed powder greenware fabrication, (ii) preparation of dense cermet with greater than 70 v/o initial ceramic content, and (iii) incorporation of non-reactive TiB$_2$ in B$_4$C/Al cermets.

1.1 Preparation

Since densification of B$_4$C/Al composites by ROC depends upon liquid metal assisted rearrangement of the ceramic particles, intimate mixing and packing of the powders was considered to be an important goal of the project. Both dry mixing and wet mixing processes were studied.

A description of the powders used in this program is given in Appendix A. Boron carbide powder was typically in the 0.1-3.0 μm diameter range (~1 μm median diameter). A high packing density boron carbide powder with a particle size range of 0.1 to 15 μm was used in some cases. The aluminum powder was finer than 325 mesh (nominal 4 μm diameter). The titanium diboride powder also had a median particle diameter of 4 μm.

Dry mixing was accomplished by combining powders in a plastic bottle with the complex rotating and tumbling motion of a Turbula Mixer (Glenn Mills, Inc.). Green pucks were pressed without binder and processed as described in Appendix A. Mixing times were optimized by qualitative inspection of parts after densification.

Development of a colloidal casting formulation for codispersed B$_4$C and Al powders has already been reported (see Appendix B). Toluene was chosen as the mixing medium in order to avoid the oxidation of Al powder that was expected in water and alcohols. A variety of short chain and polymeric additives were evaluated by sedimentation, viscosity, and filtration rate experiments for the codispersion of the B$_4$C and Al powders in 70:30 volume ratio. Sedimentation experiments indicated that the dispersion stability of fine B$_4$C powders was much more sensitive to the additive used than was the stability of the coarse TiB$_2$ and Al powders. All dispersants suitable for B$_4$C were also found to be suitable for the mixed dispersions.

Modelling of the pressure casting process by filtration theory indicated that 70:30 B_4C/Al filter cakes were incompressible below 50 psig. The filtration rate was about 5 times faster for an agglomerated suspension with Adogen 172D oleylamine than for a dispersed suspension with Hypermer KD3 polymeric dispersant, but the casting density was about 5-10% lower. Casting times for a 1.25 cm thick part were 5.5 and 33 min, respectively at 50 psig. Extrapolation of these data to a casting pressure of 500 psig predicts casting times of less than 15 min for 2.5 cm cakes, assuming that the cakes remain incompressible at this pressure.

1.2 Properties

Some degree of residual porosity (typically 1-2%) was evident in all of the ROCed composites. Parts prepared with varying B_4C content (see below) indicated that porosity was not noticably sensitive to the ceramic loading and was, therefore, not due to packing limitations of the ceramic powder. Possible reasons for this porosity are: (1) gas formation during the ROC cycle, and/or (2) formation of incompressible agglomerates from B_4C + Al reactions during the heating steps prior to ROC.

Gas formation was a significant problem in early densification experiments. Bloating and rupturing of the containment cans was frequently observed after part recovery if a hot vacuum outgassing step was not performed before ROCing (see Appendix A for experimental details). Significant H_2O and CO_2 evolution was shown to occur in TGA/MS analysis of B_4C and B_4C/Al powder compacts when heated from 25 to 650°C. The extent of gas formation depended primarily on the oxygen content of the B_4C powder and the atmosphere, and could not be entirely eliminated without resorting to very high purity non-oxidizing atmosphere, particularly above 400°C. Organic dispersants were shown to be volatilized after a single burnout cycle and were not responsible for the gas formation observed during ROC. Although gas formation was minimized by incorporation of the hot vacuum outgassing step, it has not been discounted as a cause for microstructural porosity.

It was found early in this work that reactions between B_4C and Al begin at temperatures as low as 450°C to form Al_4BC and other phases. These reactions could cause formation of rigid agglomerates prior to ROC and prevent full densification. Although the effect of reaction phases on densification has not been systematically evaluated, control of ceramic-metal reactions at low temperatures is likely to be the key to elimination of residual porosity in these materials.

The effects of different greenware processing methods on mechanical properties are indicated by the first 3 samples in Table 1. The well dispersed, wet mixing formulation with Hypermer KD3 polymeric

Table 1. Properties of ROCed Composites with 30 v/o Al Before Heat Treatment.

Sample	Density (g/mL)	Hardness (Rockwell A)	Flex Strength
70/30 B_4C/Al/dry	2.62±.03	81±3	57±5 ksi
70/30 B_4C/Al/wet/A	2.57±.02	77±5	45±20 ksi
70/30 B_4C/Al/wet/B	2.56±.02	74±5	70±10 ksi
49/21/30 B_4C/TiB_2/Al/wet/B	2.94±.01	73±5	73±15 ksi
63/7/30 B_4C/TiB_2/Al/wet/B	2.71±.01	74±5	65±12 ksi

dispersant (designated "B") gave parts with moderately higher strength than dry mixed formulations or agglomerated wet mixed formulations containing Adogen 172D oleylamine (designated "A"). Surprisingly, however, lower hardness and density were obtained with both of the wet mixed parts than with dry mixed materials.

Addition of TiB_2 particulates to the composites had no significant effect on the properties reported in Table 1. Note, however, that these data are for samples which were not heat treated after densification. Because TiB_2 is not reactive with the phases in B_4C/Al composites, one would expect heat treatment to have a different effect on TiB_2 and non-TiB_2 containing materials (see next section). Heat treatment experiments have not yet been performed for TiB_2 composites.

A high purity, high packing density B_4C powder was used to prepare B_4C/Al composites with >70 v/o initial ceramic content (see Appendix A). Greenware were prepared by wet mixing and slip casting with the Hypermer KD3 formulation. The packing limit for this B_4C powder was approximately 80 v/o. A sample made with an initial composition of 90/10 B_4C/Al was was found to have a final Al content of 20 v/o due to intrusion of the metal can during ROC. Subsequent evaluation of the part revealed cracks which had been filled with molten metal during densification. Samples with initial compositions of 70/30 and 80/20 B_4C/Al densified without significant intrusion of Al. The Rockwell A hardness increased from 74 to 77 with increasing ceramic content, while flex strength was relatively unaffected (83±5 ksi for 70/30 vs. 78±3 ksi for 80/20). Microstructural porosity in the 2-20 μm diameter range was observed in all of the compositions, independent of ceramic loading.

2.0. HEAT-TREATMENT OF DENSE B4C/AL CERMETS

The main objectives of the heat-treatment experiments were (i) determination of the conditions at which B-C-Al phases can be formed, and (ii) establishing the effect of these phases on static and ballistic properties.

The major phases influencing mechanical properties of B_4C/Al based materials are Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3 (Appendix C). Since the formation of $AlB_{24}C_4$ is associated with the existence of undesirable Al_4C_3, the heat-treatment should be limited to temperatures below 1000°C. At these temperatures AlB_2 and Al_4BC form the dominant phases. Heat-treatment conducted at temperatures between 600°C and 700°C produces mainly AlB_2, while heat-treatment at 900°C to 980°C gives mainly Al_4BC. Heat-treatment between 700°C and 900°C results in materials with mixture of AlB_2 and Al_4BC.

In order to produce samples for heat-treatment experiments, boron carbide powder was dry mixed with aluminum powder and ROCed or partially sintered prior to the ROC pressure infiltration (see Appendix A). It has been established that an increase in hardness of B_4C/Al composites depends on the kinetics of Al_4BC formation and the Al_4BC to AlB_2 ratio. At temperatures below 1000°C, the maximum hardness of 88 (Rockwell A scale), is achieved after about 20 hours of heat-treatment. The flexure strength of B_4C/Al materials depends on the continuity of the boron carbide phase (see Appendix C). A reduction in flexure strength was observed in all B_4C/Al materials experiencing heat-treatment above 600°C. It is believed that this reduction was not due to the properties of some specific phases, but rather to the phenomena associated with the process involving the growth of new phases. The increase of fracture toughness was observed only in B_4C/Al based materials with isolated grains of boron carbide. This increase was associated with densification of metal phase. The formation of ceramic phases reduces toughness in a way that depends on the type of phase formed. AlB_2 is least detrimental to the fracture toughness of B_4C/Al materials.

3.0. BALLISTIC EVALUATION

The main objective of ballistic screening was to determine potential applicability of B_4C/Al cermets for lightweight armor against small caliber threats.

The ballistic screening experiments indicate that the ballistic limit of B_4C/Al materials is directly related to the initial content of boron carbide concentration, type of phases formed in the system, and continuity of ceramic phase. It has been found that ballistic limit

increases when the amount of B_4C, AlB_2 and/or Al_4BC increases. In contrast, formation of $AlB_{24}C_4$ and Al_4C_3 was detrimental to ballistic properties. The higher the initial boron carbide content, the higher the ballistic efficiency, approaching 90% of that for hot-pressed boron carbide. The highest ballistic ratio was observed in materials containing about 80 v/o of boron carbide. B_4C/Al cermets with 70 v/o of initial boron carbide content showed ballistic efficiencies ranging from 70 to about 80%, depending on chemistry. The 10 and 30 v/o replacement of boron carbide by TiB_2 resulted in materials with slower metal depletion reactions. Because of the greater amount of residual metal, heat treated TiB_2-containing composites had ballistic efficiencies between 72 and 74% relative to hot pressed B_4C and similar to that of nonheat-treated B_4C/Al cermets. At high ceramic content, B_4C/Al materials with connected boron carbide phase showed typically 2 to 3 percent higher ballistic ratio than B_4C/Al cermets with boron carbide grains isolated in multi-phase matrix. In the latter case, the largest contribution came from AlB_2, which plastically deformed under high impact. Although, the chemistry and the continuity of ceramic phases were found to play important roles, no strong correlation between static mechanical property and ballistic performance was observed.

4.0 GRADIENT STRUCTURES

Since the ROC process allows one to densify combinations of dissimilar materials in one structure, the objective was to develop a practical process to make gradient structures of armor scale.

In order to take advantage of the full range of properties of B_4C/Al composites, a gradient composition was desired in which hard, low metal content cermet layers would be backed by tough, high metal content cermet. Pressure filter casting of stacked B_4C/Al compositions was chosen over stacked tape cast structures due to the anticipated difficulty of removing a large amount organic binder from thick armor structures. A gradient structure of five discontinuous layers which ranged from 70 v/o to 30 v/o B_4C (nominal) in a 2.5 cm thick tile was demonstrated. Samples have not been prepared for ballistic evaluation at this time.

Gradient structures were made by successive pressure casting of 0.5 cm thick layers of B_4C/Al in a stainless steel pressure filter (see Appendix A). After ROC, about half of the gradient parts had laminar cracks between the 70/30 and 60/40 B_4C/Al layers. The cause of the cracks has not yet been determined, but it is likely that they formed before or during ROC since they were filled with metal. Polished cross sections of the gradient parts had composition dependent Rockwell A hardnesses of 74±2 (70/30), 71±1 (60/40), 67±2 (50/50), 58±2

(40/60), and 47±3 (30/70). Residual porosity in the 2-20 μm diameter range was evident in the microstructure of all layers, independent of ceramic content. This observation indicates that the porosity was not due to insufficient packing efficiency of the boron carbide powder.

CONCLUSIONS

Research performed under BTI/DARPA contract DAAL 03-88-C0030 on development of B_4C/Al based composite armor allows the following conclusions to be made.

1. The developed B_4C/Al based materials are a promising alternative for the use in lightweight armor application. The advantage of B_4C/Al composite over the traditional metal armor is its ballistic limit of 80 to 90 % of that for hot pressed B_4C, thus similar to ceramics such as AlN or SiC. The advantage of B_4C/Al over monolithic ceramic armor is its higher toughness.

2. The ballistic efficiency of B_4C/Al materials, relative to hot-pressed boron carbide, was found to be directly related to the initial boron carbide content, the B-C-Al phases formed in situ, and their continuity. The highest improvement of ballistic efficiency was associated with increasing contents of B_4C and AlB_2 in the system. At the same time no strong correlation between ballistic performance and mechanical properties (i.e., fracture toughness, flexure strength, hardness, or modulus) was observed.

3. The Rapid Omnidirectional Compaction process is a suitable technique to produce nearly dense B_4C/Al cermet at the low temperature. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like structure through heat-treatment.

4. Mechanical properties of B_4C/Al cermets depend mostly on the concentration and continuity of the boron carbide phase. Colloidal processing and post densification heat-treatment can be used to further modify properties for the application at hand.

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PUBLICATIONS

1. P.D. Williams, Y.B. Huang, "Colloidal Processing and Casting of B_4C/Al Greenware," Proc. 3rd Internat. Conf. Ceram Powder Process. Sci., February 4-7, 1990 (San Diego, CA), To be published.

2. A.J. Pyzik and B.R. Beaman, " The Effect Of B-C-Al Phases On Mechanical Properties Of B_4C/Al Based Materials". To be published.

PRESENTATIONS

1. A.J. Pyzik, " The Effect Of Heat Treatment On Properties Of B_4C/Al Cermets", 3rd Internat. Conf. Ceram. Powder Process. Sci., February 4-7, 1990 (San Diego, CA).

2. A.J. Pyzik, J. Ott, K. Groves, and A. McCombs, " High Impact Behavior Of B_4C/Al Cermets", 92nd Annual Meeting of American Ceramic Soc., April 23, 1990, Dallas, TX.

Appendix A
EXPERIMENTAL CONDITIONS

POWDERS

The boron carbide powder used in most of this work was prepared on a developmental scale by a carbothermal process at The Dow Chemical Company and attrition milled to a size between 0.1-3.0 μm. Major impurities were <1 w/o free graphitic carbon, 1.0-1.5 w/o oxygen, 0.4 w/o nitrogen, 160 ppm calcium, 140 ppm chromium, 270 ppm iron, and 330 ppm nickel. The surface area was 7 m^2/g. Initial dispersion and filter casting studies used Tetrabor® 1500 B$_4$C powder from Elektroschmelzwerke Kempten ("ESK", Munich, FRG), which had physical and chemical properties very similar to those of the Dow powder. The powder obtained from ESK was supplied as 20-80 μm spherical (spray dried) agglomerates which made it undesirable for use in the dry mixed powder preparations. Subsequently, a premium grade, high purity B$_4$C powder became available from ESK which could attain a packing density of 70-80% of theoretical. This powder was used in the preparation of high ceramic content composites.

Titanium diboride was obtained from Union Carbide (HCT-F grade, nominal 4 μm diameter) with a surface area of 0.74 m^2/g. Major impurities were 0.42% carbon, 0.81% oxygen, and 270 ppm iron.

The aluminum powder, Alcan 105 grade, was a >325 mesh (nominal 4μm diameter) powder of >99% purity. Impurities (from neutron and X-ray analyses) included oxygen (0.7%), iron (0.2%), and silicon (0.1%). The surface area was 0.54 m^2/g.

All powders as supplied by the manufacturers were stored under N$_2$ atmosphere as a precaution, but could be kept in ambient atmosphere for months with less than a 0.1 w/o change in oxygen content.

MIXING AND FORMING

Dry Method

All dry powder processing used developmental boron carbide made at Dow since the spray dried agglomerates in the ESK powder were not easily broken down during mixing. Boron carbide and aluminum powders were weighed in the desired ratio (usually 70:30 by volume) and screened (35 mesh ASTM) in a nitrogen-filled glove box in order to protect the metal powder from ambient atmosphere during agitation. The blend was loaded into a polypropylene bottle under N$_2$ and tumbled with a Turbula T2C mixer from Glenn Mills, Inc. The blend was periodically removed and screened (35 mesh ASTM) to break up agglomerates generated during mixing. Total mixing time was 4 to 6 h. Binder addition was not necessary to obtain whole dry pressed parts.

Greenware was formed at 33.2 ksi in a Dake press with 3.505" diameter die. Part thickness was typically 1/2". The pressure was held for 10-15 minutes in order to de-air and reduce "spring-back" of the compact. Samples were then baked out under vacuum at 510°C for 4 h.

Wet Method

ESK Tetrabor 1500 B_4C powder was used in the dispersion and filtration rate experiments, while the internally prepared B_4C was used to make parts for ROC and subsequent property measurement. Both powders behaved similarly in the dispersion and casting process. Pucks with the composition 70/30, 80/20, and 90/10 (v/o) B_4C/Al were cast with the high packing fraction B_4C powder from ESK.

A detailed description of the casting formulations and procedures has been reported (Appendix B). Dispersions for casting were typically prepared by stirring designated amounts of B_4C, TiB_2, and Al powders into the dispersant/toluene solution to obtain 40 v/o total solids. Ultrasonic agitation (800 watts, 2.5 cm horn) and slow roll milling with SiC media were used to disperse and mix the powders. Pucks with 7.0 cm diameter were cast in a pressure filter at 50 psig. Parts of smaller or larger dimension were slip cast into covered PTFE rings on flat plaster molds. Thin (0.4-0.5 cm) cross sections of 1.5-2.0 cm thick slip cast parts were analyzed by X-ray diffraction, BET surface area, and %C, and gave no evidence for compositional gradients due to preferential settling of powders during casting. This was in spite of the fact that slip casting on plaster could take as long as 4 h for the Hypermer KD3 formulations.

Filter cast parts were dried at 45°C in air and then baked out under flowing N_2 at 500°C to remove organic additives.

DENSIFICATION

B₄C/Al Materials With B₄C Isolated In Multi-Phase Metal Matrix

Baked out greenware were enclosed in fitted cans of low carbon steel or 1100 aluminum; internal spaces between the can and the parts were filled with 1100 aluminum thin sheets and pellets. Steel cans were made slightly oversized in order to allow extra aluminum fill material to be placed between the part and the wall of the can. A metal stem was attached to a hole in the top of each can for vacuum outgassing. Canned parts were evacuated at ambient temperature for >12 h and then heated to 100, 300, and 610°C, successively, such that < 25 μm Hg pressure was attained at each temperature. The parts were cooled to ambient and the stems were sealed under vacuum.

Each sealed part was loaded into a separate fluid die and surrounded with glass pocket medium at ambient temperature. The fluid die assemblies were heated to between 655-660°C under N_2 as quickly as possible (2-3 h) to minimize $Al_xB_yC_z$ phase formation. The dies were then transferred to the ROC press and compacted at 120 ksi for 30 sec. Parts were broken out of the glass after cooling and milled out of the metal containers.

B_4C/Al Materials With Continuous Ceramic And Metal Phases

In general, the processing is similar to that for the isolated B_4C matrix, except that a sintered, porous body must first be formed from a particulate ceramic powder. The sintered, porous boron carbide body is placed in contact with the metal and heated to about 680°C to 700°C. After pressure is applied, liquid metal is forced into ceramic and fills the voids.

PROPERTY MEASUREMENT

Reported final densities were the average of the indivdual densities determined from the weights and geometric volumes of 4 point bend bars. Percent total aluminum was determined by X-ray fluorescence from a 3/8" diameter circular area on a flat cut surface of the cermet. Sample counts were calibrated by reference to an NBS standard Al sample containing Fe and Si. Four point bend tests and specimens (3 mm X 4 mm X 45 mm) were in accordance with the military specification MIL STD 1942. A minimum of 10 bars from each sample were tested. Hardness was tested using Rockwell A scale and 13.3 kg load.

BALLISTIC TESTING

Concurrent with the development of the processing technology, ballistic testing was carried out to monitor the effect of several variables on the ballistic behavior of the cermet products.

The ballistic screening was done with a two shot limiting velocity test (Vbl). The testing was carried out at University of Dayton Research Institute ballistic range. Limiting velocities were obtained to within 50 feet/sec when possible. The test projectile was a simulated .30 cal AP round (Rc=54). Targets (0.33 inch thick) were constructed by mounting the experimental tile, with epoxy resin, directly onto a 0.25 inch 6061 aluminum plate. The ballistic criteria used to evaluate test results were based on a direct comparison to hot-pressed ceramic armor tile. This comparison is reported in the form of ballistic

efficiency, i.e. the ratio of the areal density of hot-pressed boron carbide at 2700 fps to the areal density of the experimental tile at 2700 fps, as determined from the experimental Vbl.

APPENDIX B
COLLOIDAL PROCESSING AND CASTING OF B$_4$C/AL GREENWARE
P. Douglas Williams and Yi-Bin Huang

COLLOIDAL PROCESSING AND CASTING OF B_4C/Al GREENWARE

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The codispersion of fine boron carbide and aluminum powders in toluene was studied with a variety of surfactants. Dispersion stability was dominated by the higher surface area powder, which was B_4C in this case. Short chain amine surfactants were generally effective in reducing the sedimentation volume of B_4C in toluene, but still exhibited flocculated suspension characteristics (rapid settling, clear supernatant). Two polymeric dispersants were identified which yielded well dispersed, slow settling dispersions of B_4C. Casting of concentrated B_4C/Al powder dispersions (70:30 vol ratio, 40 v/o total solids) in a pressure filter at 138-345 kPa (20-50 psig) indicated that the filter cake permeability was insensitive to filtration pressure in the range studied, except when the casting rate was slow enough for sedimentation to be observed. Wet cake density was found to be sensitive to the type of additive, ~50% of theoretical for short chain surfactants and ~60% of TD for polymeric surfactants. Parts prepared from well dispersed formulations appeared to be stronger and more reliable after densification than those prepared from weakly flocculated systems.

INTRODUCTION

Tough B_4C/Al composites are attractive for structural, wear, and armor applications which require high modulus and low density.[1] The ability to prepare these composites with different B_4C/Al ratios and with a connected or disconnected ceramic phase microstructure allows a wide range of properties to be obtained.[2] In addition, reactions between the ceramic and metal phases can be exploited by annealing the dense cermet. Proper depletion of the Al and B_4C phases to form ternary $Al_xB_yC_z$ compounds yields materials with higher hardness and modulus.

B_4C/Al composites can be prepared by molten metal infiltration of porous green and sintered bodies or by a novel pressure densification process known as Rapid Omnidirectional Compaction (ROC).[3] Although recent patents have indicated improvement,[4] bulk infiltration processing is typically slow and limited in practical application to parts of < 2 cm thickness. Also, since infiltration requires temperatures above 1000°C, the formation of ternary $Al_xB_yC_z$ phases can be extensive, particularly in thick samples with long processing times. In order to optimize the

mechanical properties of the composite, it is desirable to control the formation of ternary phases.

ROC processing allows the isostatic compaction of thick B_4C/Al parts below 1000°C with better control of ternary phase formation and shorter processing time than infiltration.[5] The ROC densification of B_4C/Al composites proceeds by molten metal assisted rearrangement of the ceramic particles.[6] In order to successfully prepare dense cermets with high ceramic content (> 60 v/o) by ROC, the ceramic powder must have a high packing efficiency and must be well mixed with the metal phase. Filtration or slip casting provides excellent mixing and greenware packing, but requires a formulation in which both of the constituent powders are well dispersed.[7] This report describes the dispersion properties of fine boron carbide and aluminum powders in toluene and the analysis of their casting behavior by filtration theory. Bend strength data is presented for dense B_4C/Al parts cast from weakly flocculated and well dispersed casting systems.

EXPERIMENTAL

The boron carbide and aluminum powders in this study were used without modification.* Reagent grade toluene from Fisher Scientific was used without purification. Dispersants were used as obtained from commercial sources.** Oxygen and nitrogen analyses were obtained by fluxing a powder sample in a LECO EF-100/TC-136 electrode furnace / thermal conductivity detector. Carbon analysis was obtained by combustion in a LECO HF-100/IR-212 induction furnace / infrared detector system. Percent free carbon (as graphite) was determined from the ratio of the integrated X-ray diffraction peaks for graphite and boron carbide.[8] Particle size analysis was obtained by centrifugal sedimentation of a dilute (< 0.1%) dispersion of powder in neutral distilled water (Horiba CAPA-700).

Gravity sedimentation experiments were performed with 5 v/o solids dispersions. Powders were added to the dispersant/toluene solutions and agitated ultrasonically (300 watt, 2 cm horn) for 30 sec in a 50 mL beaker. The dispersions were then quickly transferred to a 25 mL graduated cylinder and stoppered. Some dispersants with slow powder adsorption rates (e.g. Acryloid B-99), yielded lower sediment volume when stirred for several hours between sonication and sedimentation. The cylinders were allowed to stand at ambient temperature without disturbance for at least 24 h before the final sedimentation volume was recorded. Viscosity was recorded at ambient temperature with the small sample adapter spindles #18 or #31 on a Brookfield Rheoset LVRH Viscometer. Viscosities and shear rates were calculated from the spindle constants supplied by Brookfield Engineering.

Dispersions for casting were prepared by stirring the B_4C and then the Al powders into the dispersant/toluene solution to obtain 40 v/o total solids. Ultrasonic agitation (800 watts, 2.5 cm horn) was sufficient to remove visible agglomerates

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* TETRABOR® 1500 boron carbide was obtained from Elektroschmelzwerke Kempten ("ESK", Munich, FRG). Alcan 105 aluminum powder was from Alcan-Toyo America, Inc. (Joliet, IL).
** See the Appendix for a list of suppliers.

and leave a smooth, dry film on a spatula tip. The dispersion was then roll milled for at least 16 h in a 450 mL wide mouth polypropylene bottle with 75 g of 5 mm diameter SiC balls. Pucks were filter cast on a 0.2 µm pore size PTFE membrane* in a stainless steel pressure filter.** A cylindrical 70 mm ID stainless steel insert was made and sprayed with a fluorocarbon polymer film to make part removal easier. Casting was carried out under 138-345 kPa (20-50 psig) of N_2. During casting, the filtrate was collected in volumetric glassware and measured as a function of casting time. The filtration was stopped before the liquid layer reached the top of the cake and the remaining liquid was then removed from the part by pipet. The wet cake volume was determined by mass balance of the system components, including recovered filtrate and excess disperson. The dry cake mass and geometric volume were determined after the parts had been dried at 50°C in an air ventilated oven.

Four point bending was performed on ROCed B_4C/Al test specimens (3 mm X 4 mm X 45 mm). Bend specimen preparation and test procedures were in accordance with the military specification MIL STD 1942.

RESULTS AND DISCUSSION

Powder Characterization

The B_4C powder was supplied as 20-80 µm spherical agglomerates (presumably from spray drying). The particle size distribution by sedimentation was between 0.1 - 3.0 µm (median ~ 1.0 µm). The BET surface area (N_2, 77 K) was 9 m^2/g. Major impurities included 1.3% oxygen, 0.4% nitrogen, and 0.5% residual graphite. The Al powder was a >325 mesh (nominal 4 µm diameter) powder of ~99% purity. Impurities (from neutron and X-ray analyses) included oxygen (0.7%), iron (0.2%), and silicon (0.1%). The BET surface area (Kr, 77 K) was 0.54 m^2/g. No significant increase in the oxygen content of the ceramic or metal powders was detected, even after months in ambient atmosphere.

Dispersion Properties

Because water and alcohols are corrosive to aluminum,[9] toluene was chosen as the fluid medium for dispersion. Other candidate solvents such as aliphatic hydrocarbons and ethers were not evaluated. All of the sedimentation and viscosity results reported here were obtained with ESK 1500 B_4C.

The sedimentation volume of 5 v/o ESK B_4C in toluene is shown in Table 1 for a variety of additives. A loading of 2% additive per dry weight of powder was found to be sufficient to obtain the minimum sedimentation volume for each dispersant. The most effective dispersants were considered to be those which allowed the highest particle packing or lowest sedimentation volume.

Previous study of boron carbide powders has shown the surface to be dominated by the acidic properties of a boric acid overlayer.[11,12] Inspection of Table 1

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* Micron Separations, Inc., Distributed by Fisher Scientific, Cat. No. F02-LP090.
** Fisher Scientific, Cat. No. 09-753-25E, 316 SS, 750 mL capacity, 75 mm diameter.

Table 1. Sedimentation Data for ESK 1500 B₄C (3.15g in 25 mL toluene).
Additive concentration is 1.5-2.5% vs. dry weight powder.

mg	Dispersant	Sed. Vol. (mL)
63.0	Hypermer KD3 proprietary amine-capped polyester	2.50
126.0	Acryloid B-99 50% PMMA/PBMA copolymer	3.00
78.2	Adogen 471 trimethyl tallow ammonium chloride	3.50
79.5	Alkaterge T oleyloxazoline	3.50
51.6	Emcol CC-36 polypropoxytrialkylammonium chloride	3.50
40.1	Jeffamine D-4000 aminated polypropyleneoxide, 4000 MW	4.00
70.5	Petrosul M60 60% sodium petroleum sulfonate	4.25
44.0	Adogen 349 distearyl methylamine	4.50
60.9	Emphos CS-1361 phosphate ester of ethoxylated alkylphenol	4.50
42.4	Adogen 172-D oleyl amine	4.75
46.2	Jeffamine D-2000 aminated polypropylene oxide, 2000 MW	4.75
38.9	Witcamine PA78B oleyl imidazoline salt	4.75
46.2	Adogen 142-D stearyl amine	5.00
45.3	Adogen 185 3-aminopropyl ether of C₁₂-C₁₅ alcohol blend	5.00
35.2	Varonic T-205 ethoxylated tallow amine	5.00
33.8	Witcamide 511 diethanol oleylamide	5.00
55.4	Adogen 115-D soya amine	5.25
47.5	Adogen 572 3-aminopropyl oleyl amine	5.75
42.3	Adogen 382 triisodecylamine	6.75
49.3	Adogen 163-D lauryl amine	8.50
43.8	Jeffamine D-400 aminated polypropyleneoxide, 400 MW	11.50
48.8	Kellox Z3 Menhaden fish oil	12.00
34.1	Tergitol NP-4 ethoxylated nonylphenol	13.00
33.9	Pluronic L121 ethoxylated polypropylene oxide, 4400 MW	14.00
44.0	oleic acid	16.25
33.6	Starfol OO oleyl oleate ester	18.50
	none	22.00

indicates that the most effective dispersants had excellent solubility in toluene. The presence of a basic functional group (i.e., amine, oxazoline, and imidazoline groups) which should have strong attraction for the acidic powder surface was beneficial, but of lesser importance. The series of experiments with the Adogen fatty amine additives reveals a gradual decrease in sediment volume with an increase in the number and length of the fatty tail groups bonded to the amine group. Nonionic, ethoxylated surfactants (Tergitol NP-4, Pluronic L121) were not effective, perhaps due to their relatively poor solubility in toluene. The Jeffamine polypropyleneoxide surfactants were more active due to the greater solubility of their polymer chains in toluene and the basic character of the amine capping group. The Emphos CS-1361 and Petrosul M60 dispersants with strongly ionic functional groups and excellent solubility in toluene were also very effective and indicated that functional group polarity may be more critical than acidic or basic character.[13] Additives such as fish oil, oleic acid, and Starfol OO had good solubility in toluene but were not
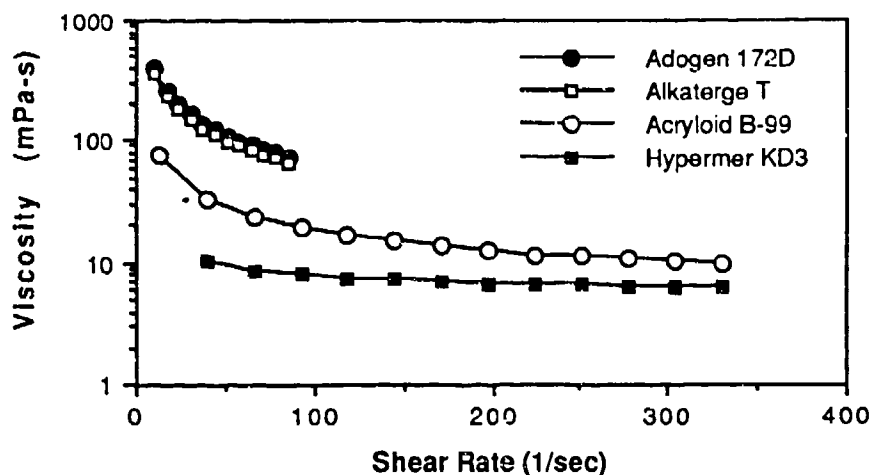
Figure 1. The Viscosity of 70/30 (vol ratio) B₄C/Al Dispersions in Toluene (35 v/o total solids, 2% dispersant vs. dry weight solids).

effective, presumably because of a combination of low molecular weight and low affinity for the acidic B₄C surface.

Three types of sedimentation behavior were observed in the B₄C experiments. (1) In the most stable dispersions a cloudy supernatant persisted throughout the experiment and a dense sediment cake grew slowly from the bottom of the tube. (2) In the least stable dispersions the entire solid mass "slumped" rapidly to its final volume and left a clear supernatant, usually within 1 h. (3) Weakly flocculated particles settled rapidly to yield a clear supernatant and then continued to rearrange and pack into a relatively dense cake. Most of the systems in Table 1, were of the latter weakly flocculated type, which Aksay and co-workers have described as "lubricated" systems.[10] Only the Hypermer KD3 and Acryloid B-99 polymeric dispersants exhibited cloudy, fully stabilized dispersions (type 1).

Sedimentation of the Al powder (3.38 g in 25 mL toluene) was relatively insensitive to the dispersant added, possibly because of the large particle size and low surface area of the powder. Settling was quite rapid and usually complete within 30 min. A sediment volume of 2.00 to 3.00 mL was obtained for dispersions with 2% of the additives Hypermer KD3, Acryloid B-99, Alkaterge T, and Adogen 172D. With no additive the sediment volume was 8.50 mL.

Dispersants for viscosity testing were selected for their sedimentation performance and low ash content (i.e., Na⁺ or Cl⁻). In accordance with the sedimentation data, the weakly flocculated dispersions containing the short chain surfactants, Adogen 172-D and Alkaterge T, were more viscous and more shear sensitive than the dispersed systems containing the polymeric additives, Acryloid B-99 and Hypermer KD3 (Figure 1).

Table 2. Casting Time and Cake Density for Filter Cast B₄C/Al Greenware (207 kPa (30 psig), 40 v/o solids, 2% dispersant).

Dispersant	Casting Time (min) (for 1.25 cm Cake)	Wet Cake Density (% TD)	Dry Cake Density (% TD)
Adogen 172D	5.6	50	58
Alkaterge T	5.0	52	60
Acryloid B-99	25.0	57	62
Hypermer KD3	33.3	62	62

Casting Properties

Filtration at constant pressure is described by[14]

$$\frac{dt}{dV} = K_p V + B$$

where $\qquad K_p = \dfrac{c\,\alpha\,\mu}{P\,A^2} \qquad$ and $\qquad B = \dfrac{R_m\,\mu}{P\,A}$

and where t is time, V is the filtrate volume, c is the mass of solids deposited per volume of filtrate collected, α is the specific cake resistance, μ is the viscosity of the filtrate, P is the total pressure drop across the filter cake and membrane, A is the cross sectional area of the filter, and R_m is the resistance of the filter membrane. Values for dt/dV were estimated as $\Delta t/\Delta V$ for adjacent points in the volume vs. time
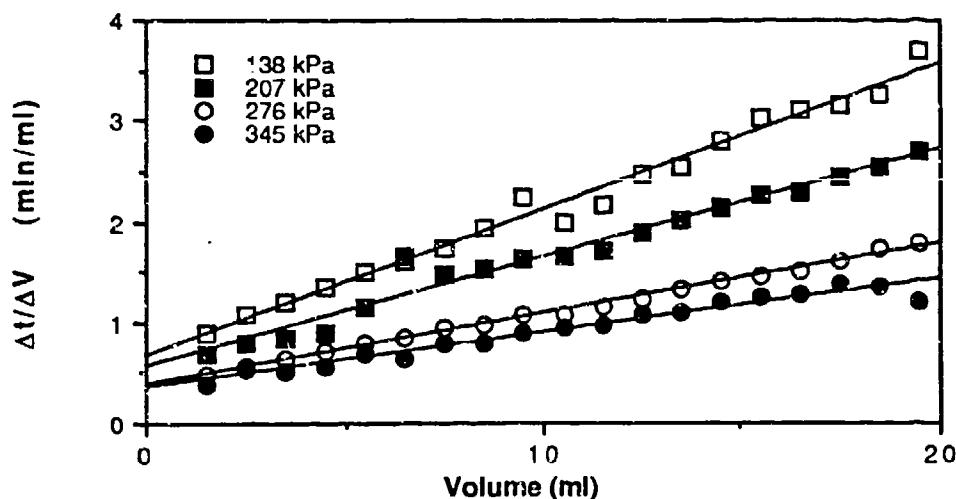
Figure 2. Filtration Rate Plot for 70/30 B₄C/Al in Toluene (2% Hypermer KD3 dispersant).
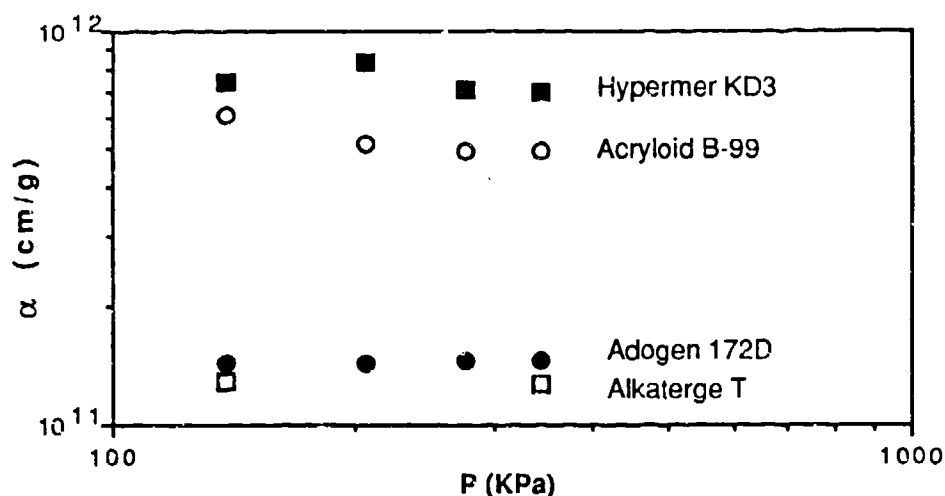
Figure 3. Cake Resistance for Filter Casting Formulations as a Function of Filter Pressure.

data. The volume V was taken to be the mean of adjacent points. The value of c was calculated from the final cake mass over the final filtrate volume. The filtrate viscosity μ was measured relative to that of pure toluene in the ULA spindle of the Brookfield viscometer.

Formulations with the polymeric dispersants, Hypermer KD3 and Acryloid B-99, required longer casting time than the Adogen 172D and Alkaterge T formulations, but resulted in higher wet packing density (Table 2). Due to the greater drying shrinkage of the parts from the Adogen 172D and Alkaterge T formulations, the final dry cake densities approached those obtained with the polymeric additives. Filter cake resistance (α) was calculated from the slope of $\Delta t/\Delta V$ vs. V for filtrations run at different pressures (Fig. 2). For a compressible filter cake, α should increase with increasing pressure. A plot of α vs. P (Fig. 3) gave no indication of cake compression in any of the formulations between 138-345 kPa (20-50 psig). The small increase in cake resistance at low pressure for the Hypermer KD3 and Acryloid B-99 dispersants was likely to be due to sedimentation since the casting time was fairly long under these conditions. Sedimentation would cause the filter cake height to increase faster than by filtration alone and, thus, result in a higher than expected specific cake resistance. As expected from the compressibility data, the density of the filter cakes was also insensitive to pressure in the range studied.

Dense Cermet Properties

Two cm thick castings of 70/30 B_4C/Al from the Hypermer KD3 and Adogen 172D formulations were heated to 500°C in nitrogen to remove the organic additives and then densified by Rapid Omnidirectional Compaction (ROC). The density of the recovered parts ranged from 2.50-2.55 g/cc and indicated residual porosity;

theoretical density depends on the amounts of ternary $Al_xB_yC_z$ phases formed, but is usually ≥ 2.57 g/cc. The cause for this porosity is still under investigation, but is probably due to gas formation during densification or insufficient packing efficiency of the B_4C powder.

Flexural strengths of the densified B_4C/Al from different casting formulations were determined without further heat treatment. Parts cast from with Hypermer KD3 dispersant had a mean flexural strength of 413 MPa ($\sigma = \pm 50$ for 13 bars), while the weakly flocculated Adogen 172D dispersant gave 310 MPa ($\sigma = \pm 140$ for 17 bars). Although the statistical significance is questionable, the more uniform mixing and particle packing in the parts prepared with Hypermer KD3 dispersant appeared to yield stronger and more reliable material.

CONCLUSIONS

The colloidal stability of the 70:30 (vol%) B_4C/Al powder dispersions in this study was dominated by the boron carbide powder because of its higher surface area than the Al powder. Short chain amine surfactants were generally effective in reducing the sedimentation volume of B_4C in toluene, but still produced flocculated suspension characteristics (rapid settling, clear supernatant). Highly stable dispersions were obtained with the polymeric additives, Hypermer KD3 and Acryloid B-99. Pressure casting of 40 vol% dispersions with 70/30 B_4C/Al slurries has been used to prepare 50-52% dense wet cakes with short chain amine dispersants and 57-62% dense wet cakes with effective polymeric dispersants. Wet cake density was found to be a much more sensitive indicator of dispersion quality than dry cake density. Analysis of volume vs. time data from pressure casting trials indicates that the wet filter cakes are incompressible for filtration pressures between 138-345 kPa (20-50 psig). Dense parts from dispersed casting formulations yielded higher mean flexural strength than those from weakly flocculated formulations.

ACKNOWLEDGEMENTS

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APPENDIX

The following additives were obtained from the manufacturers indicated: Acryloid® B-99 (Rohm & Haas, Philadelphia, PA); Adogen® 115-D, 142-D, 163-D, 172-D, 185, 349, 382, 471, 572, Starfol® OO, Varonic® T-205 (Sherex Chemical, Dublin, OH); Alkaterge® T (Angus Chemical, Northbrook, IL); Emco!® CC-36, Emphos® CS-1361, Witcamide® 511, Witcamine® PA78B (Witco Chemical, Houston, TX); Hypermer® KD3 (ICI Americas, Wilmington, DE); Jeffamine® D-400, D-2000, D-4000 (Texaco Chemical, White Plains, NY); Kellox® Z3 (Spencer Kellog); oleic acid (Fisher Scientific); Petrosul® M60 (Penreco, Butler, PA); Pluronic® L121 (BASF Wyandotte, Parsippany, NJ); Tergitol® NP-4 (Union Carbide, Danbury, CT).

APPENDIX C
THE EFFECT OF B-C-AL PHASES ON MECHANICAL PROPERTIES OF B$_4$C/AL BASED MATERIALS

Aleksander J. Pyzik and Donald R. Beaman

THE EFFECT OF B-C-AL PHASES ON MECHANICAL PROPERTIES OF B4C/AL BASED MATERIALS

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Midland, Michigan 48740

B_4C/Al cermets were fabricated using the ROC process and then post heat-treated to form multi-phase ceramic materials with a variety of designed compositions. It was found that the major phases influencing the mechanical properties of B_4C/Al based materials were Al_4BC, AlB_2, $AlB_{24}C_4$ and Al_4C_3. Because undesirable Al_4C_3 accompanies the formation of $AlB_{24}C_4$, heat-treatment should be limited to temperatures below $1000°C$. At these temperatures, AlB_2 and Al_4BC are the dominant phases. Materials with the majority of the metallic aluminum reacted to form Al_4BC had high hardness and stiffness. Heat-treatment at $600°C$ and below improved both fracture toughness and flexure strength while heat-treatment above $600°C$ reduced flexure strength. It was shown that post-densification heat-treatment can be used as a tool to improve some properties of B_4C/Al cermets, as well as to change the two-phase cermet into a multi-phase ceramic containing only a few percent of residual metal.

I. Introduction

Much research work on ceramic containing systems is devoted to studies involving the quality of starting powders, formation of greenware, and densification processes. In contrast, this paper describes boron carbide based materials whose properties can be tailored by *post-densification* heat-treatment analogous to metals. In dense B_4C/Al cermets, the aluminum metal can be largely depleted through the formation of B-C-Al phases with up to 70 volume % of the material consisting of new binary and ternary phases. While the existence of some of these phases has been reported for B-C-Al and B_4C/Al systems [1-4], the exact effect of their presence on mechanical properties is unknown.

The purpose of this work is (i) to characterize low temperature chemistry in the B_4C/Al system, (ii) to develop processing conditions leading to the formation of selected ceramic phases, and (iii) to determine the effect of these "in situ" produced B-C-Al phases on the mechanical properties.

Dense B_4C/Al materials can be achieved using infiltration[5] or, as in this work, through Rapid Omnidirectional Compaction (ROC).[6] ROC is a quasi-isostatic consolidation process in which high isostatic pressure (830 MPa) is applied for a short duration time (5-10 seconds). A powder compact is subjected to pressure delivered through a molten glass or glass-ceramic mixture which is capable of plastic flow. Some benefits provided by ROC are illustrated in the DSC scan shown in Figure 1. The Al melting endotherm at 660°C is followed by a reaction exotherm at about 700°C, a reaction endotherm at about 1010°C, and another endotherm at about 1180°C. ROC processing is done near the melting point of aluminum therein, suppressing the formation of low temperature phases while eliminating the formation of any high temperature phases. Thus, ROC provides *cermets* with limited B-C-Al phases, which can be post heat-treated to form multi-phase *ceramic materials* with a variety of designed compositions, structures and properties. The goal is to broaden the use of B4C

based material which is presently limited by difficulties in densification by processes other than hot pressing and by the extreme brittleness of B_4C.
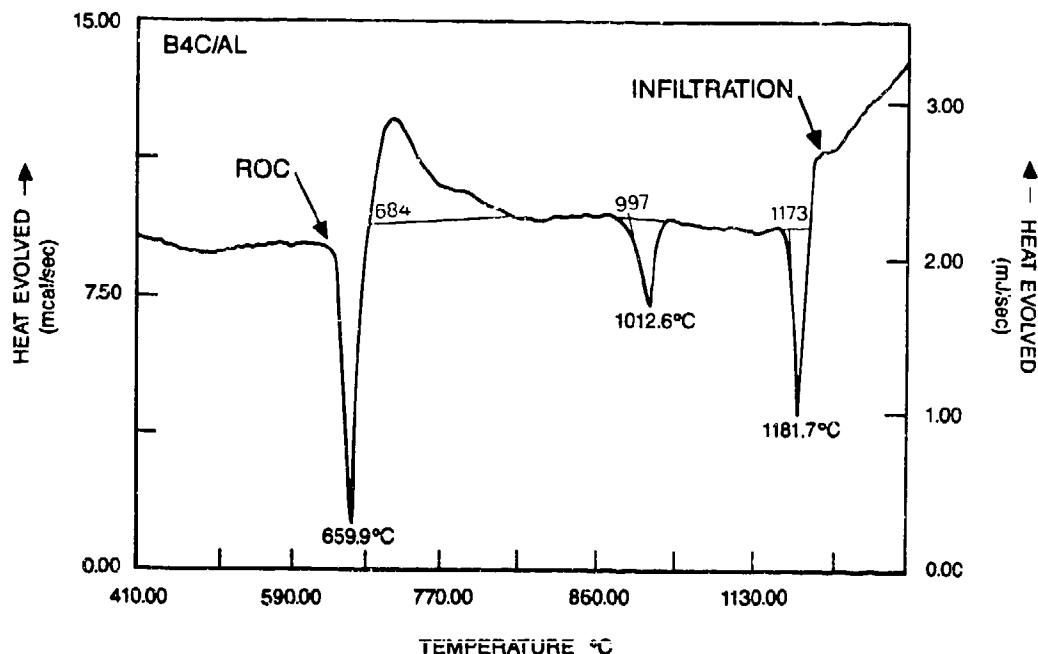

Fig. 1. DSC scan of boron carbide/aluminum powder

II. Experimental Conditions

(1) Raw materials

The boron carbide used in this study was a Dow developmental powder with 21.27 wt. % total carbon content of 21.27 %, 0.4 % free carbon , 1.27 % oxygen and a surface area of 6.8 m^2/g; the major impurities are 161 ppm Ca, 142 ppm Cr, 268 ppm Fe and 331 ppm Ni. The aluminum powder (Alcan 105) produced by Alcan-Toyo America, Inc. , contained 0.8 % Al_2O_3, 0.18% Fe and 0.12% Si and had a surface area of 0.5 m^2/g.

(2) Densification technique

Two different types of B_4C/Al were prepared. In one, the boron carbide and aluminum powders were dry mixed in a rotary blender and then pressed into 75 mm diameter discs using uniaxial compaction in a stainless steel die. No lubricants c binders were used. In the other, 75 mm diameter discs of slip cast B_4C that had been sintered to 70% of theoretical density were surrounded by aluminum metal and sealed under vacuum at 550°C in steel cans. The sealed cans were placed in fluid dies. The fluid dies with mixed B_4C and Al powders were heated in the furnace to 640°C while the fluid dies with
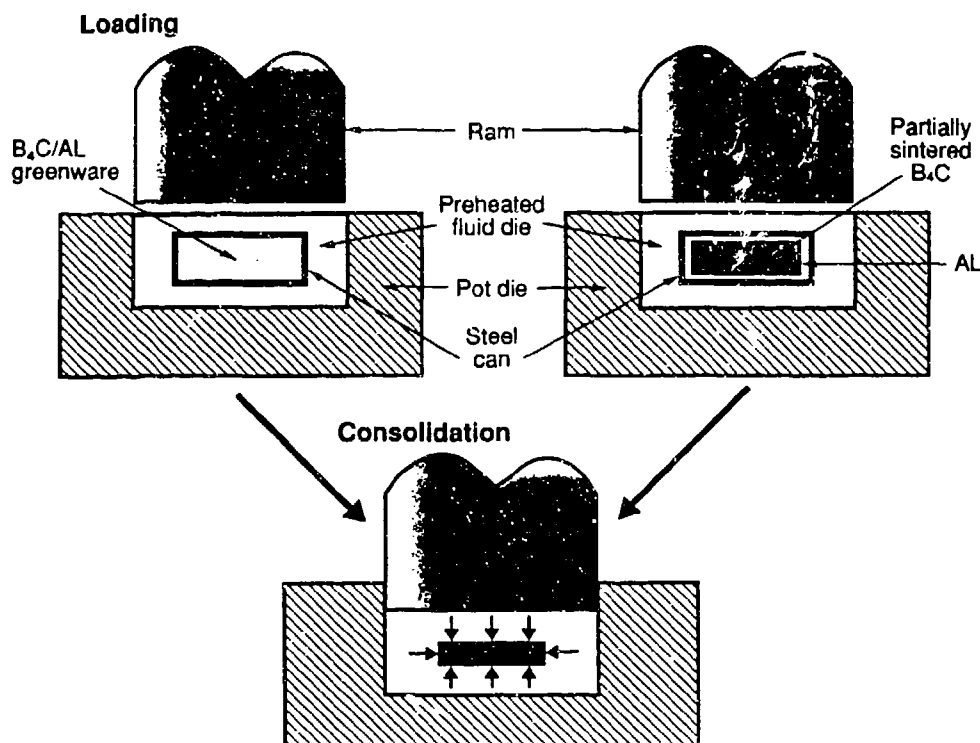
Loading

Fig. 2. Schematic illustration of the ROC densification technique

samples of partially sintered B4C were heated to about 700°C. Afte· reaching maximum temperature the fluid dies were removed from the furnace, placed in a forging press, and compacted. Schematic illustration of the ROC is presented in the Figure 2. The samples were broken out of the glass die and ground to remove residual glass. The discs were cut into various shapes for testing and characterization.

(3) Heat-treatment procedure

ROCed samples were placed in graphite boat on layer of partially sinten d boron carbide flakes and covered with thin aluminum foil. Heat-treatmen* was carried out in a mullite tube furnace under flowing argon. The heating time from room temperature to the heat-treatment temperature (450 - 1200°C) was 1 hour, while the time at the maximum temperature was 1 to 50 hours, with cooling requiring about 3 hours. In addition to ROCed samples, B4C/Al greenware was heat-treated to determine kinetics of phase formation. Boron carbide and aluminum *powders* were mixed and pressed into 24 mm diameter pellets, heat-treated for one hour in the same furnace, in flowing argon, cooled to room temperature by slow cooling at about 10°/minute, or quenching into liquid nitrogen.

(4) Characterization

The area of the aluminum melting endotherm in the high temperature DSC scan was used as a measure of the reactivity between B4C and Al at temperatures between 550°C and 1200°C. The data were collected using a Perkin-Elmer DTA 1700 interfaced to a

TADS computer. Ultra high purity argon flowing at about 10 cc/min was used as the purge gas. The samples were heated in alumina crucibles at about 20°C/min. High purity aluminum (99.999%) was used as a standard. The percent aluminum metal was given by A/B x 100, where A is the peak area in cal/g of the Al melt endotherm in the sample and B is the same for the Al standard. Precision and accuracy were about 2 percent.

Crystalline phases were identified by x-ray diffraction with a Philips diffractometer using CuKα radiation and a scan rate of 2° per minute. The chemistry of all phases was determined from electron probe analysis of polished cross-sections using a CAMECA CAMEBAX electron probe. The accuracy in the determination of elemental composition was better than 3% of the amount present.

The broken pieces from 4-point bend testing were used to measure the density in an Autopycnometer 1320 (Micromeritics Corp.) with an accuracy of 0.01 g/cm^3.

Samples for transmission electron microscopy (TEM) were prepared in the following manner: 3 mm diameter x 1 mm thick discs, cut with an ultrasonic disc cutter, were thinned to 100 μm with diamond plates and laps and finished on both sides using 1 μm diamond. Dimpling with 1 μm diamond reduced the thickness to 15 μm and the final thin section was obtained by Ar ion/atom milling from both sides using a liquid nitrogen cooled stage. 5 kV and 2-3 milliampere current.

Bulk hardness was measured on surfaces polished successively with 45, 30, 15, 6 and 1 μm diamond paste and colloidal silica suspension on a LECO automatic polisher. The Rockwell A hardness was measured using a 13.3 kg load. The Vickers microhardness of isolated phases was measured using a LECO tester and loads of 10 to 20 grams. The largest grains of a particular phase were examined in order to eliminate or minimize the contribution from adjacent or underlying material. Generally, the distance from the center of the indent to the nearest grain boundry was over twice the indent diagonal dimension. The indent diagonals were measured in an scanning electron microscope at 10000X.

Fracture toughness was measured using the Chevron notch technique and standard 4 x 3 x 45 mm samples. The notch was produced with 250 μm wide diamond blade and the notch depth to sample height ratio was 0.42. A cross head speed of 0.05 mm/minute was used in a 3 point bend fixture. The average of 5 to 7 measurements is reported. The calculations were made based on equations reported by Shang-Xian[7].

Flexure strength was determined from the average of 8 - 10 measurements on 3 x 4 x 45 mm samples and was performed according to MIL-STD-1942 standard.

III. Results and Discussion

(1) B-C-Al system

Even though at least nine ternary and binary phases have been reported for the B-C-Al system only the four shown in Figure 3 were found to form in significant quantities in this investigation.

Al4BC was first reported by Halverson et al[3] as an unidentified Phase X. In a more recent study, Sarikaya et al[8] found the crystal structure to be hexagonal and the composition to be Al4BC. Wood and Beaman found[9] that the solubility range of
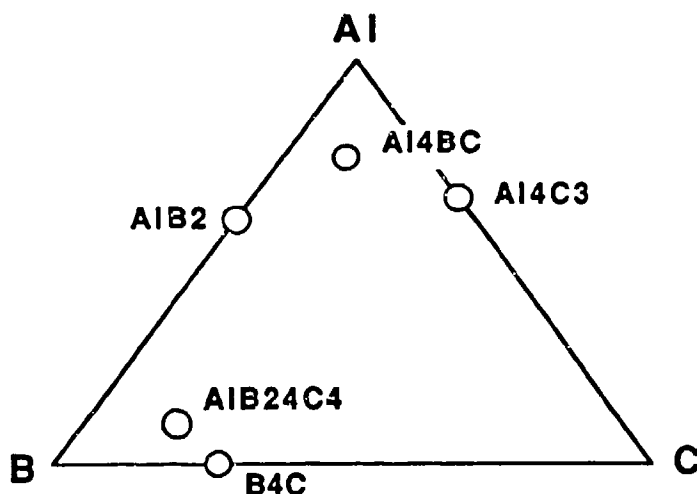
Fig. 3. Major ceramic phases in B4C/Al system (450°C to 1200°C)

aluminum in Al_4BC varied from about 69 to 84 percent. Al_4BC having typically 83 to 84% of Al is formed during initial stage of reactions, whereas heat-treatment produces Al_4BC with only 69 to 76% Al (which corresponds rather to $Al_{2.6}B_{1.8}C$ or $Al_3B_{1.2}C$ than to Al_4BC). The composition of this ternary phase lies somewhere between $Al_{2.6}B_{1.8}C$ and Al_4BC depending on the processing conditions, and shifts towards lower metal content as chemical reactions proceed. In this report, the phase is discussed as Al_4BC, notwithstanding the fact that the exact chemical composition may vary as described.

$AlB_{24}C_4$ and AlB_{10} have been identified as the same phase.[10-12] Will[13] first demonstrated the existence of $AlB_{24}C_4$ as an independent phase. Wood and Beaman[9] confirmed the formation of a phase with the chemical composition of 8% Al, 78% B and 14% C, i.e., the $AlB_{24}C_4$ composition. This this phase formed at 1000°C, well below the 1000°C to 1700°C reported by Will. The crystal structure of this phase does not correspond to high temperature $AlB_{24}C_4$ but rather to $AlB_{12}C_2$, described by Lipp and Roder.[14] Because several assumptions were made in Lipp's work which could result in chemical composition inaccuracy, it is suggested that the phase described as $AlB_{12}C_2$ is actually a low temperature polymorph of $AlB_{24}C_4$.[15] This low temperature $AlB_{24}C_4$ has a rhombohedral structure, whereas the high temperature $AlB_{24}C_4$ is ortho-rhombic.

AlB_2, the low temperature phase, has a hexagonal structure characterized by layers of metal atoms alternating with layers of boron atoms in a graphite-like structure. It has been found that the AlB_2 structure can accommodate a variety of metal atoms.[9] Experiments with a 7075 aluminum alloy (containing zinc, copper, magnesium and chromium) showed that while Zn formed a solid solution with Al, the Mg and Cr were integrated into the AlB_2 structure. Processing below 700°C gives B4C/Al based materials with AlB_2 containing 12 % of Mg and about 1.5% of Cr. Post heat-treatment at 800°C (for 10 hours) reduces this Mg to 4.5%, while the average Cr content remains at 1.2%. The Cr distribution is nonuniform.

The crystal structure of Al_4C_3 is hexagonal, and it consists of hexagonal layers of aluminum a ons interdispersed with layers of carbon atoms.[16] It has been reported[17] that evapoi.ated thin films of aluminum and carbon react above 450°C to form Al_4C_3. In B_4C/Al system, the formation of Al_4C_3 was reported above 660°C[18]; however, the boron carbide used had about 10% of free carbon making the results uncertain. Earlier work[4] indicated a rapid formation of aluminum carbide above 1200°C and negligible formation below 1000°C. The theoretical density of Al_4C_3 is 2.99 g/cm^3.[19] Four-point bend strength and Vickers hardness values have been measured at 150 MPa and 1230 kg/mm^2, respectively.[19]

(2) Phase equilibrium and kinetics of chemical reactions in B_4C/Al system

The reaction between boron carbide and aluminum starts at about 450°C with the formation of Al_4BC, but the reaction rate is slow until 600°C. Typically, at 550 to 600°C, only about 24 percent of metal can be recovered from the starting 30 volume %. This is due to the powder oxidation during mixing and reaction during heating. Above 600°C AlB_2 forms and aluminum is rapidly depleted, as illustrated in Figure 4. The open circles in Figure 4 represent the amount of unreacted Al metal retained in a B_4C/Al powder mixture after heating for one hour at temperatures between 450°C and 1200°C, and cooling to room temperature at about 10°/minute. The initial composition was 70 volume % B_4C and 30 volume % Al. The open boxes indicate the amount of unreacted metal present after quenching in liquid nitrogen. Between 600 and 700°C, AlB_2 and B_4C are the predominant phases. Above 700°C AlB_2 and Al_4BC are both present and as temperature increases the relative amount of Al_4BC increases. Between 900°C and 1000°C, the dominant reaction product is Al_4BC. At about 1000°C, AlB_2 decomposes and generates free aluminum. Heat-treatment above 1000°C produces mainly $AlB_{24}C_4$ and some Al_4C_3. These data suggest two predominant mechanisms of ceramic (B_4C) and metal depletion in B_4C/Al. Phases formed below 1000°C are

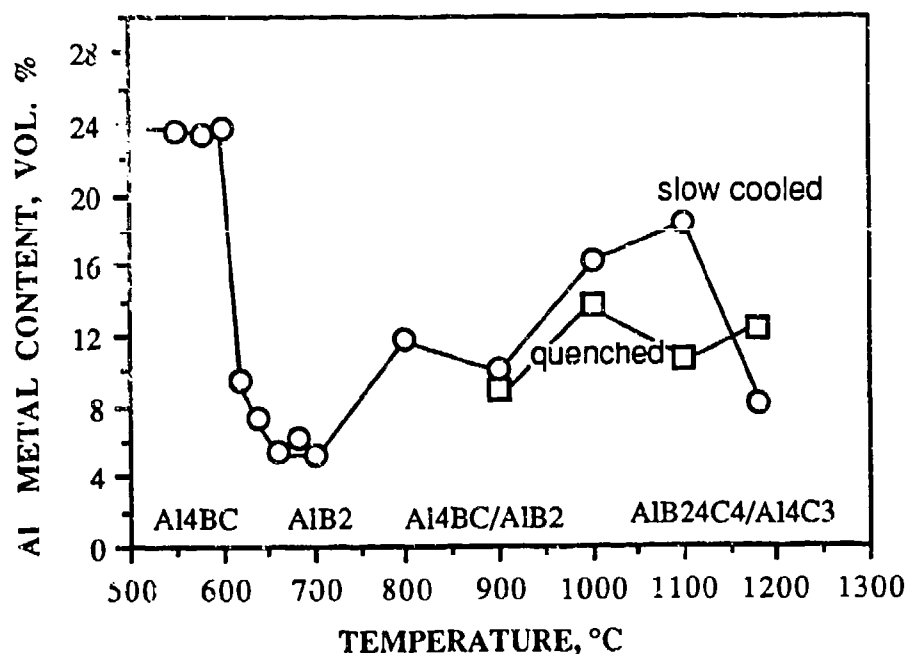**Fig. 4.** Phase formation in B_4C/Al system.

rich and their formation leads to the rapid depletion cf metal. Phases formed above 1000°C are boron and carbon rich resulting in B4C depletion and composites with larger amounts of free metal and smaller amounts of boron carbide than the same starting powders heated below 1000°C.

The cooling rate does not affect the composite composition for temperatures below 900°C, but materials quenched in liquid nitrogen from above 900°C contain less free metal than slowly cooled ones due to the formation of metastable phases above 900°C. During slow cooling, these phases decompose and release additional aluminum.

While the heat-treatment kinetics differ for B4C/Al powder mixes and previously densified B4C/Al composites, the same phases are produced. B4C/30 vol.% Al materials densified by ROCing at temperatures between 640°C and 700°C typically contain 16 to 22 vol.% of unreacted metal. Large ROCed samples (75 mm x 12 mm) undergoing slow cooling, contained 16 3% unreacted metal. In ROCed and heat-treated materials, the amount of Al metal is minimized at 900°C (Figure 5). Heat-treatment above 900°C -1000°C yields aluminum rich cermets. Heat-treatment at 1000°C produces materials with a higher content of aluminum than obtained at lower temperatures, including the solid state reaction at 600°C. This is due to the formation of phases rich in boron and carbon and deplete in aluminum. Figure 5 shows that the reactions proceed faster during first 2-3 hours of heat-treatment. At 600°C and 1000°C, equilibrium is reached after about 20 hours. The initial increase in metal observed at 1000°C is caused by the decomposition of AlB$_2$. Heat-treatments at 700°C and 900°C require more than 50 hours to reach equilibrium and the depletion of metal beyond 20 hours is slow. The amount of unreacted metal after about 50 hours at 900°C is less than 4 vol.%.
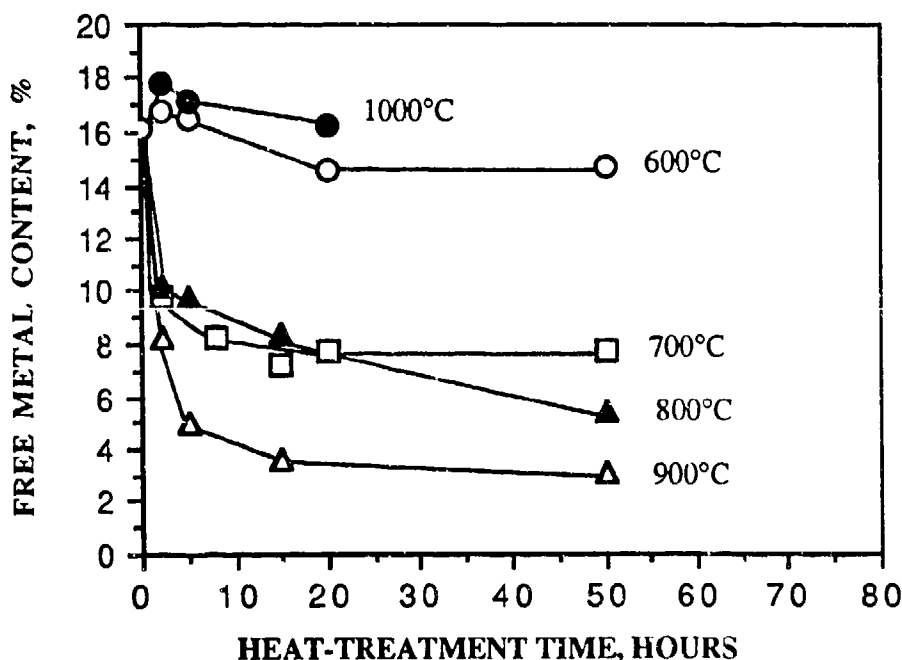

Fig. 5. The kinetics of metal depletion in post heat-treated dense B4C/Al.

(3) Microstructure

The microstructures of ROCed B_4C/Al can range from isolated grains of boron carbide in a continuous aluminum matrix to interpenetrating networks of B_4C and metal. Figure 6 shows these two types of materials after heat-treatment at 800°C for 20 hours. Aluminum is mostly depleted. In both cases B_4C, AlB_2 and Al_4BC are predominant phases, however, their spatial distribution, size and connectivity vary.
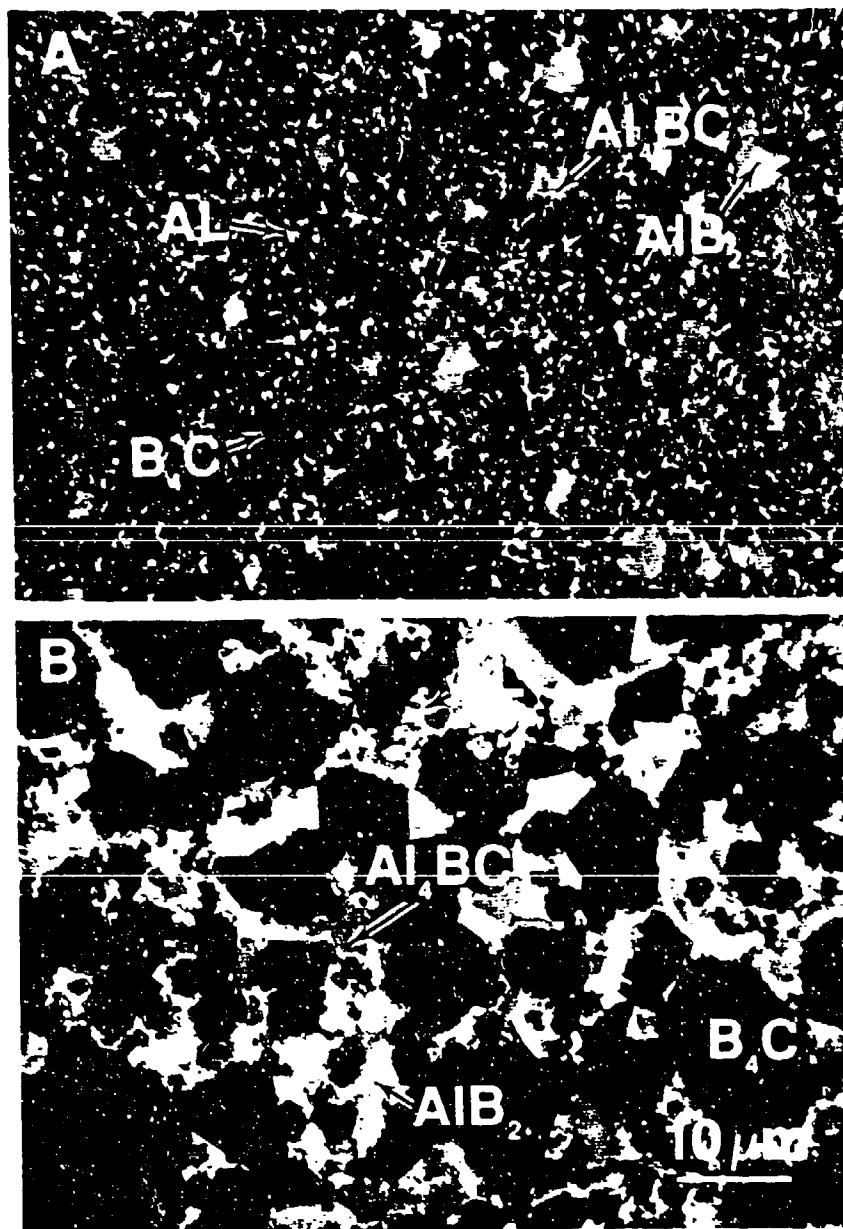

Fig. 6. The microstructures of ROCed 70 vol.% B_4C/Al with isolated grains of boron carbide (A) and with interpenetrating networks of B_4C and metal (B) after 20 hours heat-treatment at 800°C.

As described above, the phase type and content will depend on the densification temperature and post-heat-treatment time. Table I presents a phase description, useful in microstructural characterization.

Table I. Description of phases in B4C/Al based system

Phase	Optical microscopy bright field	SEM/ Back scattered electron image	Comments
B4C	grey	black	usually surrounded by blue-gray Al4BC
Al	white	white to light grey	
AlB2	yellow	grey	various shades if contains Cr
Al4BC	blue-grey; lighter than B4C	medium to light grey	
AlB24C4	slightly lighter grey than B4C	slightly lighter colored than B4C	
Al4C3	light grey	light grey	discolors rapidly in air

Metal impurities may result in the formation of additional phases and /or alter the chemistry of aluminum. Copper forms bright crystals of $CuAl_2$. Iron reacts with silicon to form FeSi. Cr and Mg are incorporated into the AlB2 structure. Zn forms a solid solution with Al but evaporates when heated above 600°C .

(4) The effect of B-C-Al phase equilibrium on the mechanical properties of B4C/Al based composites

Hardness

The mechanical properties of many B-C-Al phases are unknown with the exception of some microhardness data.[14, 19, 20, 21] The microhardness values measured herein together with literature data, are presented in Table II. The order from hardest phase to least hard is: B4C and AlB24C4 > Al4BC> AlB2> Al. The Rockwell A hardness as a function of temperature and time are shown in Figure 7. After densification, B4C/30 vol.% Al material has a hardness of about 81. Post-densification heat-treatment at 600°C and 1000°C provides a maximum hardness value of 83 , which remains stable for extended times. At 1000°C, the hardness declines initially due to the decomposition of AlB2, but then increase again as Al4BC is formed. Heat-treatments conducted at 700°C, 800°C, 900°C and 1100°C produce a maximum in the hardness versus time curve. The higher the temperature, the less the time required to obtain maximum hardness. This behavior, characteristic of the B4C/Al system, is again due to the kinetics and B-C-Al phase equilibrium. Below 1000°C, in the initial stage of heat-treatment, hard Al4BC is favored, but with increased time, there is insufficient aluminum available and softer AlB2 forms decreasing overall hardness. Between 600°C and 1000°C Al4BC and AlB2 are both present. Increases in the AlB2/Al4BC ratio lower the maximum hardness and
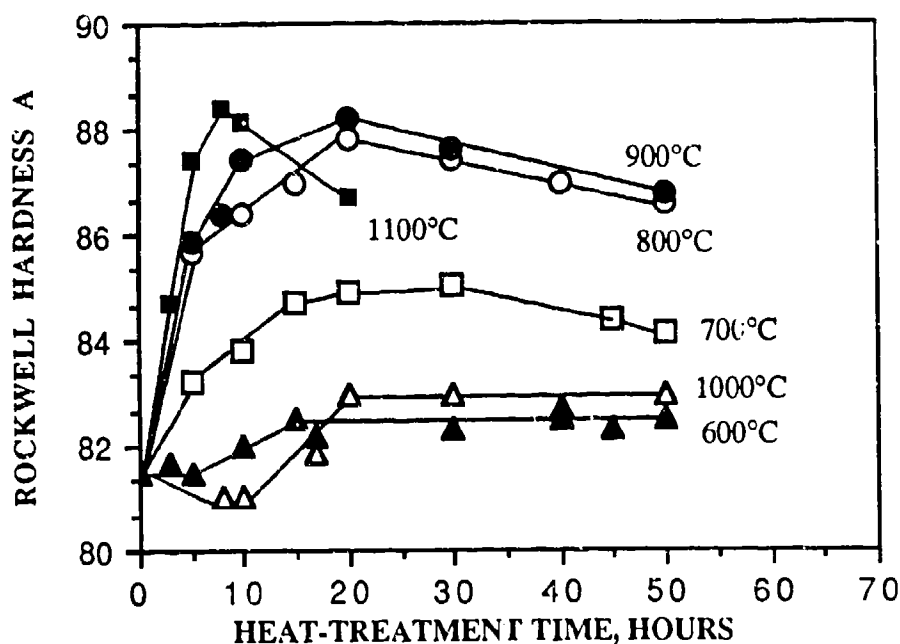
Fig. 7. The effect of temperature and time on the Rockwell A hardness of ROCed and heat-treated B4C/Al.

make the transition from rising to declining hardness more gradual. After 20 hours of heat-treatment, the AlB_2/Al_4BC ratio is 8, 0.7 and 0.4 at 700, 800 and 900°C respectively. At 1100°C, Al_4BC and then $AlB_{24}C_4$ forms resulting in a high hardness composite. However, after 8 to10 hours of heat-treatment, Al_4C_3 become the predominant new phase and the hardness declines. The highest hardness values were achieved through heat-treatments of 10 hours at 1100°C (H_{RA} =89), 20 hours at 900°C (H_{RA} = 88) or 20 hours at 800°C (H_{RA}=88).

Table II. Hardness of some phases in B-C-Al system.

Phase	Hardness (kg/mm^2)		
	Present investigation		Literature data
	2 g load	10 and 20 g load	
B4C	----	3220	3250-3350[21]
Al	88	125	19[20]
Al4BC	1310	1400	---
AlB2	860	1050	980[20]
AlB24C4	3100	----	2530-2650[14]
Al4C3	—	1254	1230[19]

Flexure strength of B₄C/Al cermets

The flexure strength was measured in B4C/Al with continuous networks of boron carbide and aluminum and also in samples where the B4C grains were isolated in a aluminum matrix. Figure 8 shows that the flexure strength of the former microstructure is higher over the entire temperature range, presumably because both phases can carry the load and the boron carbide phase is under higher compressive stress. In addition, the difference in flexure strength may be partially due to the 1 to 2 % density difference between two types of microstructure. Typically, the flexure strength of B4C/Al decreases with increasing heat-treatment temperature or time at temperature (Figure 8). B4C/Al with continuous boron carbide have constant strengths from room temperature to 600°C (540 MPa). Between 600 and 800°C, the strength decreases to a minimum of 410 MPa.

In B4C/Al composites with isolated boron carbide grains, the strength increases slightly for heat-treatment up to 600°C and then decreases sharply to 300-350 MPa.
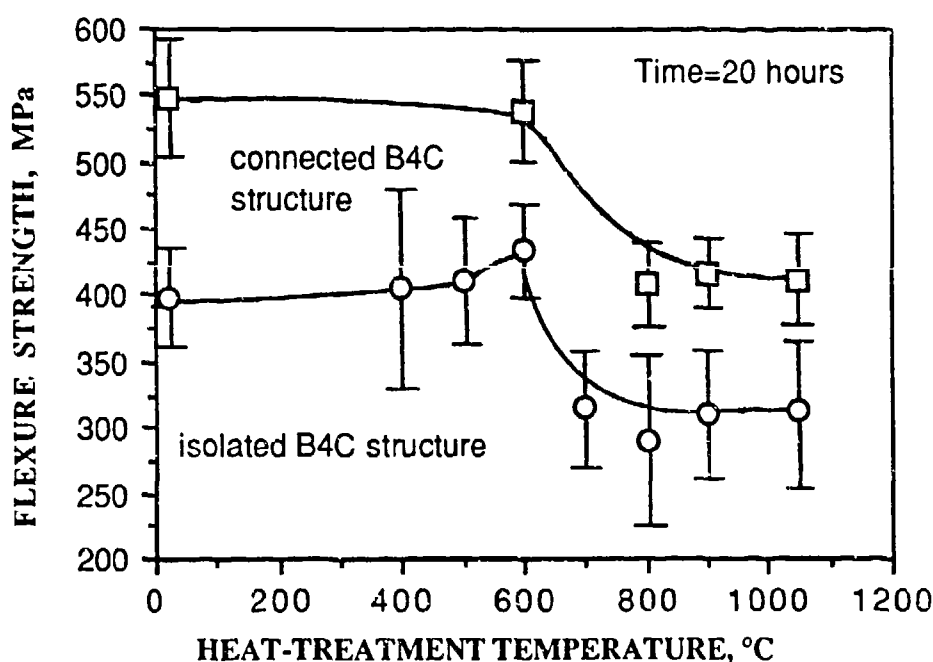

Fig. 8. The effect of heat-treatment temperature on the flexure strength of B₄C/Al composites.

Flexure strength increases from 400 MPa to 435 MPa during the first 20 hours, but then declines (Figure 9) for samples heat-treated at 600°C. This behavior is due to competing mechanisms: metal sintering and the relaxation of ROC induced stresses increases strength during the first 20 hours while the formation of new ceramic phases reduces strength at longer times. For heat-treatments above 600°C, the strength decreases continuously to 300 to 350 MPa regardless of the amount of metal. This decrease is not due to the formation of specific ceramic phases, but rather to phenomena associated with forming new phases in a material, e.g., microcracking.
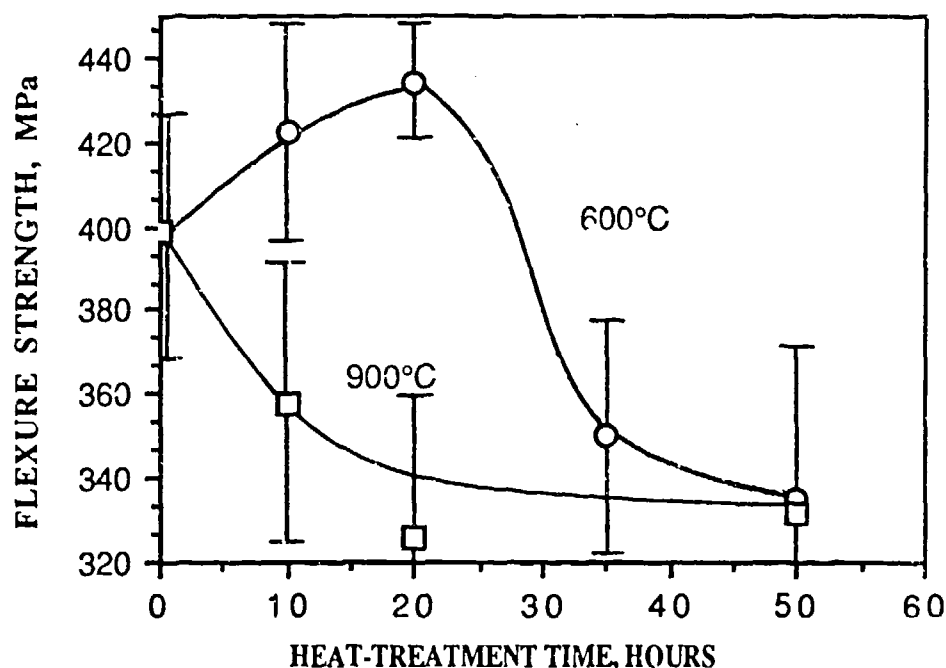
Fig. 9. The effect of heat-treatment time on flexure strength of B4C/Al composites.

Fracture toughness of B4C/Al cermets

The values of the fracture toughness of many B-C-Al phases are unknown. However, the damage and cracking pattern in the indented phases indicates that AlB$_2$ has a higher toughness than Al$_4$BC or AlB$_{24}$C$_4$ (Figure 10). Aluminum containing small ceramic crystals deforms plastically. The damage in AlB$_2$ represents shear deformati$)$n rather than brittle cracking. B$_4$C and AlB$_{24}$C$_4$ usually behave similarly, even though, in some cases, the crack propagates through the AlB$_{24}$C$_4$ and stops at the boron carbide grain boundry (Figure 10 D). Al$_4$BC shows brittle behavior (Figure 10 C) with several cracks running from the corners and sides of the indent.

Published [22-24] fracture toughness values for B$_4$C/Al range from 6 MPa m$^{1/2}$ to 16 MPa m$^{1/2}$. This variation is due to material differences, including the amount of metal, composition of the Al alloy and metal distribution as well as the shape, size and connectivity of the ceramic phases. In addition, problems are caused by the difficulty in obtaining stable crack growth. In this work, the Chevron notch technique did not produce stable crack propagation in all samples. Low fracture toughness was associated with unstable cracking whereas high toughness was associated with stable cracks. Thus, the true K$_{IC}$ values for the more brittle materials are probably lower than reported.
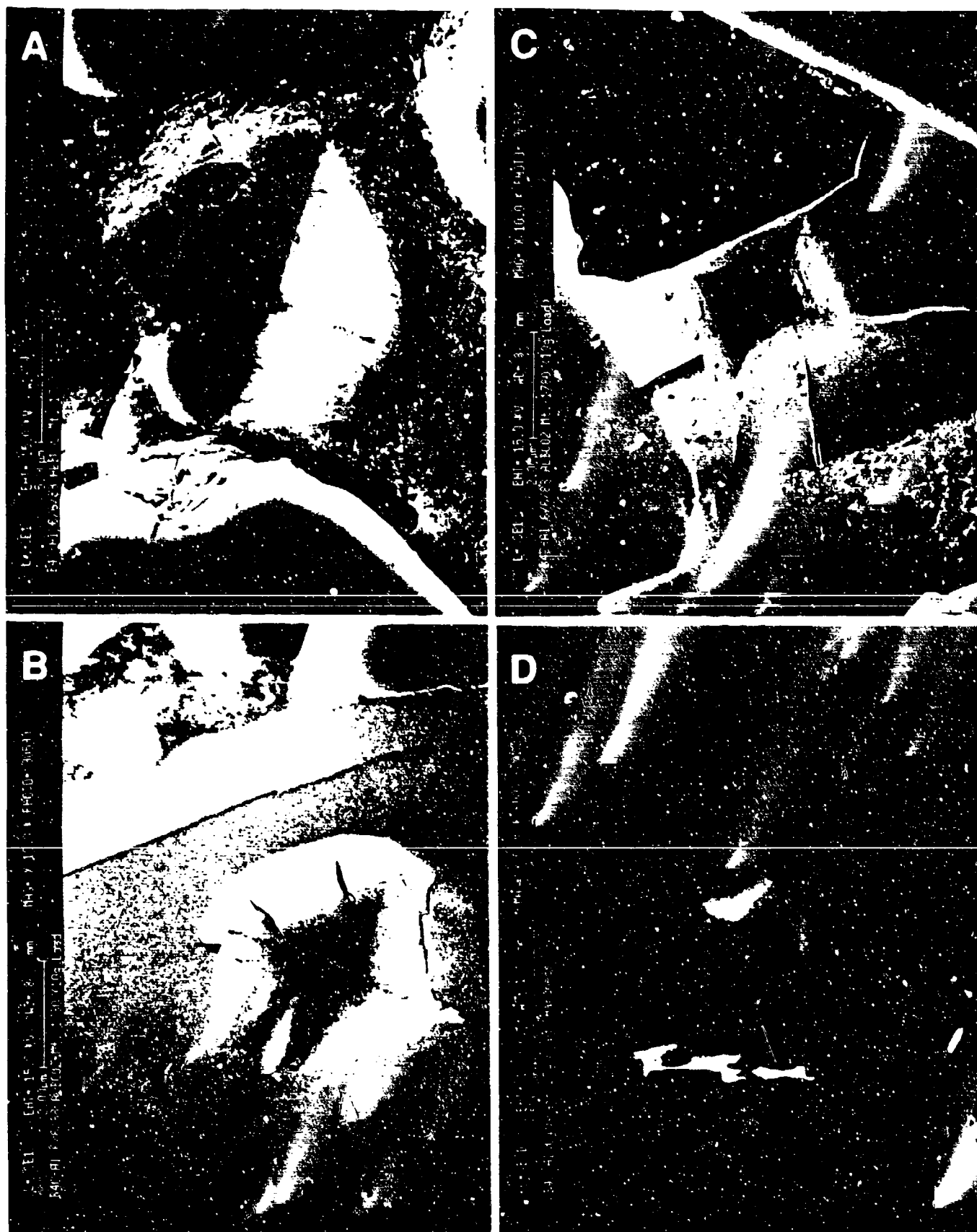
Fig. 10. Damage observed in the indented crystals of Al (A), AlB$_2$ (B), Al$_4$BC (C), and Al$_4$BC (D).

The results in Figure 11 indicate that post-densification heat-treatment can substantially improve the fracture toughness. The increase is observed only in materials containing isolated grains of boron carbide. In continuous boron carbide structures, K_{IC} decreases slowly as a function of additional heat-treatment. Because B_4C/Al composites with highly continuous boron carbide structure are chemically more stable, after heat-treatment they contain more residual free metal than B_4C/Al composites with isolated ceramic phases.[5] The fact that materials with more ductile phase have lower K_{IC} values indicates that the toughness is controlled mainly through the boron carbide phase. Therefore, optimization of the connectivity in ceramic preform would be more effective in improving the fracture toughness than changing the chemistry of the metal through heat-treatment.

In composites with isolated grains of boron carbide, K_{IC} increases over the entire heat-treatment range when compared to the as-ROCed material. Beyond the maximum at about 600°C, K_{IC} decreases. Analytical transmission electron microscopy did not reveal any differences (e.g. precipitation) between the as-ROCed and heat-treated metal phases.
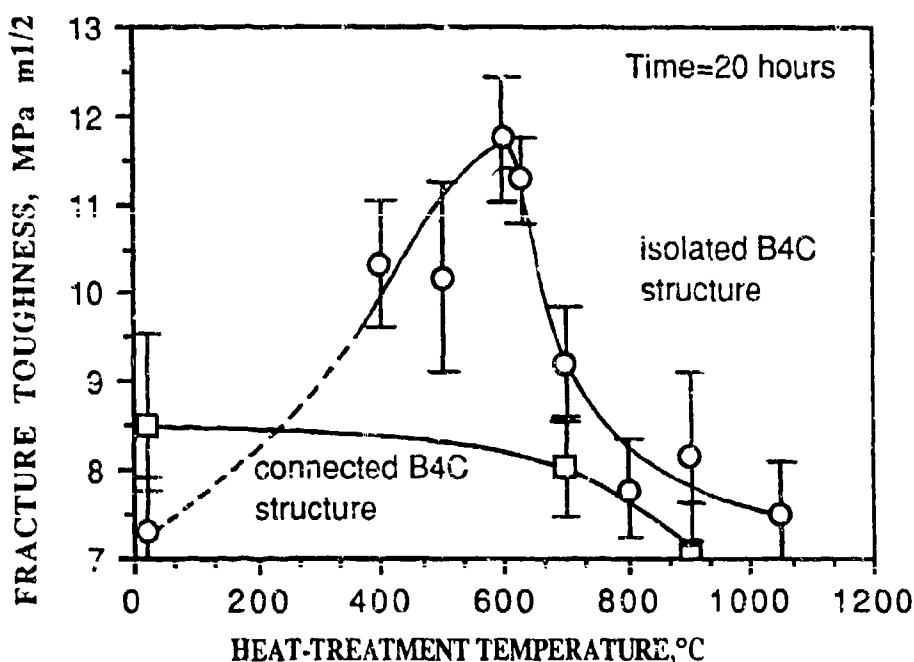

Fig. 11. The effect of heat-treatment temperature on fracture toughness of B_4C/Al composites.

However, a reduction in porosity was observed in the heat-treated samples implying increased density and improved bonding between the ceramic and metal which would account for the increased fracture toughness. At 600°C, where the highest fracture toughness was obtained, sintering of the metal takes place before significant quantities of new phases are formed. The formation of new ceramic phases reduces toughness. The extent of this reduction depends on the type of phases formed. The materials containing AlB_2 have higher K_{IC} values than those with Al_4BC and $AlB_{24}C_4$. It is certainly important to note that all the investigated B_4C/Al materials have at least twice the fracture toughness of pure boron carbide.

IV. Microdesigning Of Material's Properties

It is evident that post-densification heat-treatment can be used to improve many properties of B_4C/Al cermets by changing the cermet into a multi-phase ceramic material containing only a small amount of residual metal. Heat-treatment between: 600°C and 700°C produces mainly AlB_2; 700°C and 900°C results in a mixture of AlB_2 and Al_4BC; 900°C and 980°C gives mainly Al_4BC; and 1000°C and 1050°C results in $AlB_{24}C_4$ with small amounts of Al_4C_3 if heating does not exceed five hours.

Table III. The effect of heat-treatment on properties of B_4C/Al materials with isolated boron carbide in metal matrix.

Property	After ROC densification	After heat-treatment above 900°C to produce:			After heat-treatment at 600°C
		AlB_2	Al_4BC	$AlB_{24}C_4$	
Density g/cm^3	2.57	2.63	2.70	2.62	2.58
Flexure strength (MPa)	419	357	351	312	434
Fracture toughness (MPa m$^{1/2}$)	7.23	9.21	8.17	7.52	12.7
Young modulus (GPa)	254	290	310	280	260
Bulk modulus (GPa)	138	167	175	156	140
Hardness Rockwell A	81	85	88	88	81
Poisson's ratio	0.23	0.21	0.20	0.20	0.23

From the kinetics at each of these temperatures (see Figure 5), it is possible to produce B_4C/Al composites with different phases but similar amounts of residual unreacted aluminum. Table III compares the mechanical properties of as-densified and heat-treated B_4C/Al composites. The highest hardness and modulus can be obtained in Al_4BC containing samples. While these materials have improved toughness relative to the as densified materials, it is only about 8.17 MPa m$^{1/2}$. On the other hand, AlB_2 containing samples exhibit increased fracture toughness (9.21 MPa m$^{1/2}$), but only slight hardness (from 81 to 85) improvement. Because the AlB_2/Al_4BC ratio can be

changed and controlled by heat-treatment between 700°C and 900°C, the properties of B4C/Al composites can be selected for a specific application. Processing below 1C)°C allows the formation of large amounts of AlB2 and avoids the formation of Al4C3.

In heat-treating below 600°C, the new phases form in limited amounts and a multi-phase ceramic is not produced. The resultant B4C/Al cermets are characterized by a microstructure of isolated boron carbide grains in an aluminum matrix with improved fracture toughness and fracture strength (Table III).

V. Conclusions

1. B4C/Al cermets represent a category of chemically incompatible materials where post-densification heat-treatment permits tailoring of their chemistry and material properties. Dense, but soft, cermets can be near-net shaped and then changed into hard, ceramic-like material through heat-treatment.

2. The major phases influencing the mechanical properties of B4C/Al based materials are Al4BC, AlB2, AlB24C4 and Al4C3. Because the formation of AlB24C4 is associated with the existence of undesirable Al4C3, the heat-treatment should be limited to temperatures below 1000°C where AlB2 and Al4BC are the dominant new phases.

3. The hardness of B4C/Al ceramic composites depends upon the kinetics of Al4BC formation and the AlB2 to Al4BC ratio. At temperatures below 1000°C, the maximum hardness of 88 (Rockwell A scale) is achieved after about 20 hours of heat-treatment.

4. The flexure strength of B4C/Al ceramic composites depends on the continuity of the boron carbide phase. The highest strength was observed when boron carbide and aluminum were both present as continuous phases. A reduction in flexure strength was observed when the heat-treatment was completed above 600°C. It is believed that this reduction is not due to the presence of a specific phase, but rather to phenomena associated with the process of growing new phases e.g., microcracking.

5. An increase in fracture toughness was observed only in materials with isolated grains of boron carbide. This increase was associated with densification of the metal phase. While the formation of ceramic phases reduces toughness, the extent of this reduction depends on the type of phase formed. AlB2 is the least detrimental.

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